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AN EVALUATION OF THE DISSOLUTION PROCESS OF NATURAL URANIUM ORE AS AN ANALOGUE OF NUCLEAR FUEL

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by

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AN EVALUATION OF THE DISSOLUTION PROCESSES OF NATURAL URANIUM ORE AS AN ANALOGUE OF NUCLEAR FUEL

A report by V.H. Stern, Geological Consultant, under contract to the Atomic Energy Control Board.

ABSTRACT

The assumption of congruent dissolution of uraninite as a mechanism for the dissolution behaviour of spent fuel was critically examined with regard to the fate of toxic radionuclides. The fission and daughter products of uranium are typically present in spent unreprocessed fuel rods in trace abundances. The principles of trace element geochemistry were applied in assessing the behaviour of these radionuclides during fluid/solid interactions. It is shown that the behaviour of radionuclides in trace abundances that reside in the crystal structure can be better predicted from the ionic properties of these nuclides rather than from assuming that they are "controlled" by the dissolution of uraninite. Geochemical evidence from natural uranium ore deposits (Athabasca Basin, Northern Territories of Australia, Oklo) suggests that in most cases the toxic radionuclides are released from uraninite in amounts that are independent of the solution behaviour of uranium oxide. Only those elements that have ionic and thus chemical properties similar to U^{4+}, such as plutonium, americium, cadmium, neptunium and thorium can be satisfactorily modelled by the solution properties of uranium dioxide and then only if the environment is reducing.

RÉSUMÉ

L'hypothèse que la dissolution congrue de l'uraninite comme mécanisme pour comprendre la dissolution du combustible irradié a fait l'objet d'une analyse critique en ce qui a trait au sort des radionucléides toxiques. Les produits de fission et de filiation de l'uranium sont présents typiquement à l'état de traces dans les barres de combustible irradié non retraité. Les principes géochimiques des éléments à l'état de traces ont été appliqués pour évaluer le rendement de ces radionucléides durant les interactions entre fluides et solides. On a pu montrer que le rendement des radionucléides à l'état de traces qui se trouvent dans la structure des cristaux peut être mieux prévu à partir des propriétés ioniques de ces nucléides plutôt qu'en supposant qu'ils sont «contrôlés» par la dissolution de l'uraninite. Les preuves géochimiques tirées des gisements d'uranium naturel du bassin de l'Athabasca, des territoires septentrionaux de l'Australie et d'Oklo laissent supposer que, dans la plupart des cas, les radionucléides toxiques s'échappent de l'uraninite en quantités indépendantes du rendement de la solution d'oxyde d'uranium. Seuls les éléments qui ont des propriétés ioniques, et donc chimiques, semblables à U^{4+}, comme le plutonium, l'américium, le cadmium, le neptunium et le thorium, peuvent être étudiés de façon satisfaisante d'après les propriétés de solution du bioxyde d'uranium et seulement si le milieu est réducteur .

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1. INTRODUCTION

CANDU (**CAN**adian **D**euterium **U**ranium) reactors use fuel rods that are composed of pressed UO_2 pellets that contain ^{235}U in natural ratios with ^{238}U. After use, the spent unreprocessed fuel is stored in temporary facilities. The need for a more permanent solution to the disposal of spent fuel has prompted research in Canada to focus on deep burial in geologic formations, primarily the Canadian Shield (Aikin et al., 1977). Knowledge of the fate of the toxic radionuclides in spent fuel is necessary for an adequate safety analysis of the geologic burial of these wastes. This report investigates the assumption of congruent dissolution of spent unreprocessed fuel by examining the published scientific literature on uranium ore bodies. The questions asked in this report are:

1. Is it valid to model the dissolution of fuel rods by the dissolution of uraninite (the major uranium bearing mineral in natural ore bodies)?

2. Does the mineral uraninite dissolve congruently? and

3. What is the effect of groundwater chemistry on the mechanism of uraninite dissolution?

These questions are the first step in understanding the fate of toxic radionuclides (e.g. ^{90}Sr, ^{99}Tc, ^{129}I, ^{137}Cs, ^{226}Ra, ^{237}Np, ^{239}Pu, and ^{241}Am). The answers will determine which nuclides should be of concern in migratory processes and will help in modelling dissolution processes.

The terms "congruent" and "incongruent" are loosely used in the waste management literature, particularly in regards to disposal of nuclear fuel. From a strict mineralogical and thermodynamical viewpoint, congruent dissolution describes a process whereby the mineral dissolves stoichiometrically into solution. During congruent dissolution, there are no secondary phases formed from reaction of the initial mineral with the fluid. Incongruent dissolution, on the other hand, describes a mineral that reacts with the fluid to form a second mineral in addition to releasing some major elements into solution as dissolved species. The fluid can be an aqueous solution or a magma whose composition is known, but knowledge of the speciation of the fluid is not implied or necessary to distinguish the behaviour of dissolution. An example of congruent dissolution would be calcite dissolution, where $CaCO_3$ (solid) dissolves to Ca^{2+}(aqueous) + CO_3^{2-} (aq) with the dissolved species in the same stoichiometry as the mineral. An example of incongruent dissolution would be $Al_2Si_2O_5(OH)_4$

(kaolinite, s) + $5H_2O$ (liquid) reacting to $2Al(OH)_3$ (gibbsite, s) + $2H_4SiO_4$ (aq). It is important to note that congruent and incongruent dissolution refer to reactions between solid phases and solvents that can be written as balanced equations. In distinguishing between congruent and incongruent dissolution the emphasis is on the behaviour of the mineral phases which can be identified. It is not common or practical to define these terms with respect to the speciation of the elements in the solvent. The important concept is that the elements in the solid phase either enter solution stoichiometrically or they do not. The terms "congruent" and "incongruent" have meaning only for the particular elements that participate in the reactions. The use of the terms congruent and incongruent is not meaningful when applied to elements that are not constrained by the stoichiometric relationships of reaction equations, such as trace elements (a full discussion of these concepts is in section 4).

In the context of spent fuel disposal, where UO_2 is the dominant phase, the term congruent is used to describe the release of radionuclides in the same proportions to uranium as they were in the original uraninite. Incongruent behaviour implies differential loss of radionuclides from the mineral with respect to uranium. While the use of the terms congruent and incongruent has some use in the concepts of nuclear waste disposal, it must not be assumed that there is a known stoichiometric relationship between the radionuclides in the fuel and the fluid, as there is between the major elements such as uranium in uraninite and the fluid. In the latter case a balanced reaction can be written such as $UO_2(s) + H_2O = UO_2OH^+(aq) + H^+$. The concentration of UO_2OH^+ in the fluid is constrained by the stoichiometry of uraninite. The trace elements, however, are not constrained by the stoichiometry of uraninite. The assumption of a stoichiometric relationship could lead to false conclusions concerning the fate of radionuclides especially those that are in trace quantities with respect to the major elements uranium and oxygen. In order to avoid ambiguity, question #2 should be rephrased more explicitly:

2. Are the radiogenic and fission produced elements that result from radioactive decay and fission processes preferentially leached from uraninite?

This report summarizes the geological evidence of uraninite dissolution from natural orebodies in both reducing and oxidizing environments and includes a discussion of the differential mobility of radionuclides. The mineralogical and thermodynamic constraints on uraninite stability are also considered.

2. MINERALOGY

Uraninite is isostructural with fluorite (CaF_2), the oxides ThO_2, CeO_2, PrO_2, PuO_2, AmO_2, and the high temperature polymorph of ZrO_2 (Steacy and Keaman, 1978; Frondel, 1958). It is an isometric structure in the crystal class (4/m 3 2/m). The uranium ions are in 8-fold coordination with O^{2-} ions and the O^{2-} ions are in 4-fold coordination with the U ions (Frondel, 1958; Deer, Howie, and Zussman, 1977). The uranium in uraninite is largely in the quadravalent state (see chemical analyses 1-6, Table 1), however, there is invariably some portion of the uranium that is in the hexavalent state. It has been suggested that the oxidation of U^{4+} to U^{6+} is accompanied by excess oxygen occupying the vacancies in the fluorite structure at (½00). Filling of these vacancies would theoretically allow the U-O series to extend from UO_2 to $UO_{2.75}$ without destruction of the crystal structure (Frondel, 1958).

Elements that show chemical similarities to U^{4+} and thus are likely to enter in solid solution in uraninite are Ce^{4+}, Th^{4+}, Pr^{4+}, Pu^{4+}, Am^{4+}, Np^{4}, and to a lesser degree Zr^{4+}. The similarities in oxidation state, electronegativity, and ionic radii are due to similar electronic configurations. However, on oxidation of U^{4+} to U^{6+} the similarities in valence and ionic radii no longer exist. The uranyl ion $(UO_2)^{2+}$ is capable of forming compounds that have no analogues with Ce, Th, Pr, Np, Pu, Am, or Zr. Table 2 lists the daughter and fission products of uranium with their oxidation states and ionic radii. Those elements that have similar oxidation states, ionic radii (within ± 15%), and crystal structure are more likely to enter into solid solution (Stanton, 1972). Differences in oxidation states may be mitigated by coupled substitutions. Differences in structural states while limiting solid solution do not inhibit interstitial solution. Interstitial solution is more favourable for ions with small radii (Stanton, 1972).

The primary minerals that contain uranium as an essential constituent (see section 4) are uraninite, pitchblende, brannerite, uranothorite, davidite and coffinite (see table 3 for chemical formulas). Frondel (1958) states that uraninite is the proper name for all UO_2, with pitchblende designating a variety that lacks Th and REE's. The relationship between uraninite and pitchblende is similar to that of quartz and calcedony (Frondel, 1958) whereby pitchblende lacks an organized crystal lattice. In the literature, uraninites are usually formed in a magmatic or high temperature hydrothermal environment (e.g. pegmatitic) and have relatively high abundances of Th and REE's. They are crystalline and often massive. It is likely that the high temperature environment favors crystallinity. In contrast, the crystalline variety of pitchblende forms from aqueous hydrothermal fluids of moderate to low temperature (e.g. diagenetic fluids).

The depletion of Th and REE's may reflect the chemistry of the precipitating solutions rather than structural control (Frondel, 1958; Fryer and Taylor, 1987). The amorphous variety of pitchblende characterized by colloform banding, shrinkage cracks, and impurities is likely to have precipitated from colloidal suspension.

The secondary minerals are produced by hydration of the uranyl (U^{6+}) ion. Examples are carnotite, tyuyamunite, uranophane, thucolite, and sklodowskite. The hydrated form of coffinite is included as a secondary mineral. Table 3 lists the primary and secondary mineralization of uranium bearing compounds, accessory minerals that contain uranium, and mineral associations of uranium ore deposits.

The spent unreprocessed fuel rods consist of UO_2 pellets that have possibly experienced structural damage due to their history in a reactor as well as post reactor handling (Brookins, 1984). Microprobe analyses (Table 4) of irradiated UO_2 have shown the presence of exsolution phases (Bradbury et al., 1965 and Jeffery, 1967). These precipitates contain Mo and Ba as oxides and Te, Ru, and Rh as metals in ratios predicted by fission product yield (Jeffery, 1967).

3. THERMODYNAMIC CONSTRAINTS

Uraninite has a large stability field at low Eh potentials (reducing environments) that spans the pH range of natural groundwaters. At normal pHs and low Ehs the solubility of uranium is less than 10^{-4} ppb (Langmuir, 1978) At intermediate Ehs and neutral to alkaline pHs the presence of phosphate or carbonate in groundwater enhances the solubility of uraninite by several orders of magnitude.

Secondary uranium-bearing minerals that result from the oxidation and hydration of uraninite include sabugalite, saleeite, and torbernite (in the autunite group) and uranophane. The stable alteration products at high Eh, when dissolved phosphate or silicate is present, are the autunite group or uranyl silicates (e.g. uranophane). Langmuir (1978) calculated the solubility of the uranyl minerals. In general these minerals are least soluble at pHs between 5 and 8. The minimum solubilities of uranyl silicates and autunites are on the order of 100 ppm.

The stability of uraninite appears to favor congruent dissolution of UO_2 in the strict mineralogical and thermodynamical sense. In the absence of significant quantities of dissolved silicate, vanadate, and phosphate, under oxidizing conditions the major elements of uraninite would be expected to dissolve congruently. The presence of significant dissolved silicates, phosphates, and vanadates, however, increases the stability of uranyl minerals and favors precipitation of secondary uranium-bearing minerals. The result is incongruent dissolution of UO_2. This does not imply that the individual trace elements (e.g. decay or fission products of uranium) will behave "congruently" or "incongruently" in tandem with the UO_2. The behaviour of the trace elements are governed by their crystal chemistry independent of the major elements (see section 4 for a more detailed discussion).

4. CONGRUENT AND INCONGRUENT DISSOLUTION

As reported in section 2, the mineral uraninite is a uranium oxide, with the uranium composed of the radioactive isotopes ^{238}U (normally with an abundance of 99.2743%), ^{235}U (0.7200%), and ^{234}U (0.0057%). In nature, uraninite can accommodate impurities in its crystal lattice during initial crystallization, such as thorium, the rare earth elements, and calcium. The impurities present are dependent on the composition and temperature of the solution and on the properties (e.g. ionic radius, valence) of the element entering the crystal lattice. After crystallization of uraninite, radioactive decay of uranium produces numerous daughter products (e.g. ^{234}U, Th, Ra, Rn, and Pb) whose abundances are a function of time. If fission occurs, as in the case of a natural reactor or from anthropogenic spent fuel, fission products are also produced (e.g. ^{129}I, ^{90}Sr, ^{135}Cs, etc.) that may or may not be accommodated in the uraninite structure. Furthermore, the alpha-decay of uranium may damage the uraninite structure and may lead to instability of certain elements. When uraninite is subject to conditions of dissolution and/or reprecipitation at some stage after initial cystallization, the behaviour of minor elements with respect to UO_2 in uraninite defines their behaviour as congruent or incongruent.

If the ratios of the minor elements (present initially, or produced by the decay of parent nuclides over time or by the fission of U) with respect to UO_2 remain unchanged in uraninite during dissolution, then the process may be described as congruent dissolution. If the minor elements enter into solution in proportions to uranium that are different from their proportions in the host uraninite, then dissolution is said to be incongruent. In the following discussion this definition will be used except where specified. An alternative description that is common in the literature defines congruency on the basis of *rates* of release of radionuclides. In this definition if a radionuclide is released from uraninite into solution at the same rate as uranium it is referred to as congruent dissolution. If, however, the rates of release are different from uranium then it is said to be incongruent dissolution. This definition will be used in a specific argument. In modelling the dissolution of radioactive waste, it is common to assume that dissolution of minor elements is somehow "controlled" by the dissolution of the uraninite structure, that is, dissolution is said to be congruent. The implication of this statement is that by knowing the stability and solubility of UO_2, one can predict the stability and solubility of other chemical components in uraninite. In the following discussion, it will be shown that the behaviour of elements in uraninite other than U may be governed and predicted by chemical principles which are well-known from other geochemical treatments in the literature. It appears from these principles

that, in fact, there are very limited conditions in which other elements should apparently behave sympathetically with uranium.

To understand if an element will behave congruently or incongruently, it is important to identify whether the element is a trace element, an intermediate element, an essential structural constituent (ESC) in uraninite (Hanson and Langmuir, 1978), or an element which resides interstitially in the uraninite lattice. A trace element is an element whose abundance in uraninite is not determined by stoichiometry, and which can vary widely without any affect on the stability of uraninite. Trace elements are usually in the part per million (ppm) or parts per billion (ppb) range in minerals, and in natural uraninite could include Pb, Ra, Th, and the rare earth elements, etc..

An essential structural constituent is an element whose abundance in uraninite is determined by the stoichiometry of the mineral, such that its abundance cannot vary outside a very limited range without affecting the stability of the crystal. Essential structural constituents are always the major cations, occurring in weight percent. An example of an essential structural constituent would be Zr in zircon ($ZrSiO_4$). It is not possible to change the molar concentration of Zr in the structure within a very limited range without causing the zircon structure to become unstable. Similarly, U may be considered an essential structural constituent of uraninite in certain circumstances because it may not be possible to change its concentration in uraninite without causing instability of the crystal.

An intermediate element is one whose behaviour is intermediate between a trace element and an essential structural constituent, and whose concentration in a mineral may vary between certain stoichiometric limits. These elements usually occur at the weight percent level. An example would be Mg and Fe in olivine $(Mg,Fe)_2SiO_4$. For uraninite, it is possible that uranium could be an intermediate element if sufficient Th is available for substitution, but the total U and Th content must be close to one mole fraction.

To illustrate why it is important to know the type of element, consider a uraninite crystal composed of UO_2 and Pu, the latter at the ppb level. If this uraninite is in equilibrium with a fluid, there will be partition coefficients $K_U = [U]_{ur}/[U]_{fl}$ and $K_{Pu} = [Pu]_{ur}/[Pu]_{fl}$, where $[i]_j$ = concentration of element i in mole or weight units within phase j, ur = uraninite, and fl = fluid. The partition coefficients are similar to equilibrium constants or solubility products, but are applicable for systems in which balanced reactions may not be known. For conditions of constant pressure, temperature, redox state, pH, and fluid composition, K_U and K_{Pu} may be constant. For U,

which occurs as an essential structural constituent in uraninite and a trace element in the fluid, $[U]_{ur}$ is fixed at one mole fraction. Since K_U is constant, the concentration of uranium in the fluid ([U]) is also constant and is equivalent to $[U]_{ur}/K_U$. The concentration of uranium in the fluid cannot vary unless K_U changes. For example if the Eh of the system changes then the partition coefficient K_U would change as well as the concentration of uranium in the fluid. For Pu, which occurs as a trace element in both uraninite and fluid, the concentration of Pu is not constant in uraninite, and could vary over orders of magnitude in abundance. Since K_{Pu} is constant, the concentration of Pu in the fluid ($[Pu]_{fl}$) can also vary over an equivalent range, i.e. $[Pu]_{fl} = [Pu]_{ur}/K_{Pu}$.

Thus, if K_U is known, it is possible to predict the concentration of uranium in the fluid, as U is buffered in the fluid by the stoichiometric control of uraninite. In contrast, even if K_{Pu} is known, it is not possible to specify the concentration of Pu in the fluid without also knowing the concentration of Pu in uraninite. Thus, the Pu content of the fluid depends critically on the Pu content of the uraninite, but is independent of the uranium content of the uraninite. This means that it is not possible to predict the relative concentrations of U and Pu in a fluid in equilibrium with uraninite without knowing the partition coefficients for U and Pu and the concentration of Pu in the uraninite.

Elements that may not be contained in the crystal lattice of uraninite are those produced by nuclear processes that have sizes and charges that are incompatible with the uranium site in the crystal, or that are dislodged by alpha recoil. Such elements might include (roughly from most to least incompatible in uraninite): I, Cs, Mo, Tc, Ru, Cd, Xe, Rb, Tl, Ra, Ba, Pb, Sr, Sn, Zr, La (see Table 2). It is critical to know whether an element resides interstitially because the behaviour of such an element may not be governed by crystal-chemical controls.

As well as a knowledge of the type of element involved in the solution process, for predicting the mobility of an element it is also important to know the stability or instability of the host uraninite. Under highly oxidizing conditions the uraninite structure will become unstable when oxidation of the U^{4+} ion to the 6+ valence exceeds the tolerance of the crystalline lattice to incorporate interstitial oxygen for charge balancing. Instability occurs because U is an essential structural constituent or an intermediate element of uraninite, and the structure can tolerate only limited change in the proportion of U^{4+} present.

If the uraninite structure is unstable, all ions in the uraninite structure including trace elements and intermediate elements would enter into the

surrounding solution in the same proportions that existed in the uraninite (i.e. the process of dissolution is congruent) as long as the uraninite crystal did not react with the fluid. If, however, the unstable UO_2 structure could react with the fluid to form a new mineral structure (i.e. hydrated uranyl complexes), it would not be necessarily true that all other elements beside uranium would dissolve congruently.

Thus, under oxic conditions, there may be at least two mechanisms of dissolution of uraninite, one in which the uraninite crystal is dissolved stoichiometrically, and another in which it is in reaction relationship with the fluid. It must be clearly understood that these solution mechanisms imply that the uraninite structure is not in a state of equilibrium with the fluid. In order to understand the behaviour of elements including uranium under these conditions, knowledge is required of: a) whether the element is a trace element, an intermediate element, or an essential structural constituent; b) how the dissolution is occurring, by stoichiometric dissolution or by reaction relation; c) the solubility of the element in the fluid, uraninite, and any reaction products; d) the concentrations of trace elements in the phases being considered; and e) the kinetic factors of the process, including the rates of diffusion of elements in uraninite, the rate of reaction at the crystal/fluid interface (Berner, 1981), and the rate of fluid flow at the reaction boundary (i.e. the fluid/mineral mass ratio).

To illustrate the complexity that may exist in trying to predict how an element may behave, consider an example of the element Pu in a uraninite crystal subject to oxic conditions. In natural uraninite, plutonium (Pu) is usually at the ppm or ppb level, and can be considered a trace element. Let's consider a case where uraninite is in reaction relation with the fluid, such that UO_2 in the uraninite is reacting with the fluid to form secondary hydrous uranyl compounds. In this discussion the *rates* of nuclide release will be assessed consistent with the definition of congruent and incongruent dissolution that is based on rates of release rather than ratios of nuclides. Assuming that the fluid would accept more uranium into solution, there could be a net transfer of uranium to the fluid, the rate of transfer being dependent on the rate of the reaction forming the secondary mineral and rate of mass loss of uraninite. The behaviour of the element Pu with respect to uranium would depend on their relative affinities for the secondary mineral. If Pu was less compatible in the secondary mineral than uranium was in the secondary mineral, then Pu would be preferentially released into solution relative to uranium. However, if Pu was more compatible in the secondary phase than uranium, then U would be preferentially released into solution relative to plutonium. Thus, whether or not Pu behaved similarly to U during dissolution would depend on the type

of secondary mineral formed, the fluid composition, and the trace element compatibility of the secondary mineral.

Now let us consider a situation in which the uraninite crystal is in equilibrium with the surrounding fluid, which would occur under reducing conditions. The UO_2 in the structure would not be in reaction relationship with the fluid, and, by definition, there would be no net loss of UO_2 from the crystal. Nevertheless, there might exist a trace element such as Pu which may not be in equilibrium with that same fluid. If there was a greater chemical potential of Pu in the uraninite compared to the fluid, Pu could be released into the fluid. This process would continue until the equilibrium concentrations of Pu were achieved in the uraninite and fluid. In this case, the release of Pu would not depend on the solubility of UO_2 in the fluid. The rate of release of Pu would be governed by its rate of diffusion to the surface of the crystal and to surface reactions at the crystal/fluid interface. Because the stability of the uraninite host is not dependent on the presence or absence of Pu, the loss of Pu would not affect the stability of the uraninite structure.

Because the release of trace elements from uraninite is governed by a host of variables, as discussed above, which may or may not lead to a correlation with release of UO_2, it cannot be assumed that the behaviour of a particular trace element will correlate with UO_2. Trace elements with very similar electronic and chemical properties as U would be expected to behave similarly, but these are relatively few (under reducing conditions Th^{4+}, Np^{4+}, Pu^{4+}, Am^{4+}, Cm^{3+}, $REEs^{3+}$; under oxic conditions possibly Np, Pu, Am if they are oxidized to a higher valence).

Congruent dissolution may be observed for intermediate elements in uraninite undergoing dissolution, but again, only under certain conditions. Any secondary phase formed by reaction with a fluid would have to accommodate the intermediate elements in similar proportions to uranium as the original uraninite, otherwise preferential loss of intermediate elements from the solid phases would occur. The most favourable conditions for congruent dissolution for trace elements and intermediate elements would occur upon stoichiometric dissolution of uraninite under oxic conditions, in which all elements are dissolved directly into solution. Elements which did not reside in the uraninite structure but within interstitial sites would probably show no correlation with uranium, and these may include decay and fission products of uranium.

5. EVIDENCE FOR ELEMENT MOBILITY

In this section, consideration will be given to the evidence that the natural analogues detailed in Appendix A provide on congruent versus incongruent dissolution of uraninite. Among the various methods available to assess the solution mechanisms of uraninite and associated minor elements in a natural setting are the textural and temporal relations of uraninite and other minerals, the chemical compositions of these minerals including major and trace element and isotopic compositions, and the chemical and isotopic composition of groundwaters.

5.1. Mineralogy

Mineralogical evidence for dissolution mechanisms requires systematic documentation of the minerals present, and their textural, chemical, and temporal relationships. Unfortunately, there are few instances in the literature where such careful documentations are available. Two notable exceptions are the descriptions of Rabbit Lake by Rimsaite (1977, 1978, 1979) and of Koongarra by Snelling (1978) and Dickson and Snelling (1978). Accordingly, the following discussion will focus upon the evidence from these locations, supplemented with evidence from other less well-studied bodies. The reader is directed to Appendix A for detailed descriptions of these deposits.

The major limitation encountered in attempting to apply mineralogical observations to the question of congruent and incongruent dissolution is the lack of comprehensive geochemical studies of ore bodies. The data required include quantitative trace element and isotopic analyses of uranium and gangue minerals and their associated groundwaters. The number of studies for which data are available are few, and generally Pb is the only trace element for which interpretations can be made. This results in a heavy reliance on lead mobility to infer preferential loss of trace elements from uraninite for most ore deposits. The exceptions are the Oklo natural reactors for which numerous isotopic analyses of uraninite and whole rocks are available. Comprehensive trace element data on ore and gangue minerals from diverse geochemical settings are badly needed in order to make further interpretation of element mobility.

5.1.1 Rabbit Lake

Rabbit Lake hosts several generations of uraninite/pitchblende and secondary mineralizations of triuranium heptaoxides, Pb-bearing masuyite-becquerelite, vandendriesscheite, and wöelsendorfite, kasolite, uranophane, sklodowskite, and boltwoodite (see Table 3 for chemical formulas). The presence of several generations of pitchblende which appear to have grown

by remobilization of former generations of pitchblende, and the presence of a large diversity of secondary minerals in this deposit are first order observations indicating that there has been chemical redistribution at the site of the deposit. The succession of pitchblende generations indicates periods of stoichiometric dissolution and reprecipitation. Also observed are psuedomorphic replacement of pitchblende by hydrated oxides of U and Pb and uranyl carbonates. These observation suggest that some pitchblende was in reaction relationship with the fluids. The U-Pb oxides and uranyl silicates were in turn weathered to form uraniferous phyllosilicates and montmorillonitic clay minerals.

Chemical analyses of successive generations of pitchblende from Rabbit Lake (#1-6 of Table A1.1) indicate a trend of decreasing Pb abundances, reflecting the time available to generate radiogenic lead and systematic loss of lead to fluids as the new generations grew. The fourth generation of pitchblende is associated with radiogenic galena, suggesting that the lead lost from pitchblende was accumulated by galena. This observation indicates the preferential loss of Pb with respect to uranium during dissolution of pitchblende, and is strong evidence of incongruent behaviour for Pb. The timing of lead loss is discussed in section 5.3 on U-Pb geochronology.

The formation of secondary minerals as reaction products upon pitchblende from Rabbit Lake provide semi-quantitative evidence of incongruent dissolution. An example is the alteration of pitchblende to the hydrated uranyl silicate kasolite $Pb(UO_2)SiO_4 \cdot H_2O$. The molar Pb/U ratio in kasolite from the deposit is close to one, which is higher than the ratio in the first generations of pitchblende. This is further evidence of incongruent dissolution of pitchblende, in this case during reaction relationship with the fluid. Although not analyzed, it might be predicted that elements similar to Pb^{2+}, such as Ca, Sr, and Sn, and those similar to Si^{4+} may be retained in kasolite in a similar manner as Pb, and thus might also be expected to have dissolved incongruently. As indicated in the discussion above on trace elements (section 4.1) there is no compelling reason that these elements should be incorporated in the new mineral in the same ratios with respect to uranium as they were in the initial pitchblende. The abundances of the trace elements in the kasolite and fluid will be a function of their activities in these phases.

5.1.2 Koongarra

The Koongarra deposit preserves additional evidence of dissolution of uraninite by reaction relationships. The secondary mineralizations that are found include incomplete replacements of uraninite by the oxides curite,

fourmarierite, and vandendriesscheite, and the silicates kasolite, sklodowskite-uranophane. Snelling (1980) describes the alteration of a uraninite vein that is zoned by vandendriesscheite, fourmarierite, curite, and sklodowskite. Similar to the Rabbit Lake deposit, the formation of kasolite and sklodowskite with high Pb/U ratios may be evidence of incongruent dissolution of uraninite.

5.1.3 Cigar Lake

The Cigar Lake uranium ore deposit is an example of an ore deposit whose current environment can be described as reducing. There is little evidence of secondary, hydrated uranium minerals. Uranium loss at present is thought to be negligible as demonstrated by the low total concentrations of uranium (2 to 12 μg/l) in the present day groundwater (see analyses 79, 79B, 91A in Table A1.3). Despite the lack of apparent secondary mineralization, galena occurs associated with pitchblende, and contains high radiogenic Pb to common Pb ratios. It appears that although uraninite may have been stable, there was evidently preferential accumulation in galena of Pb derived from uraninite. It must be concluded that Pb was mobile at some stage in the history of this deposit, whereas, it appears that U was immobile. If this is true, then clearly dissolution of Pb was incongruent. In this regard, Cigar Lake, Rabbit Lake, and Koongara are just examples of deposits which contain galena with excess radiogenic Pb. The uraninites at the Carswell structure and Oklo are also associated with galena, although the isotopic composition of the lead has not been reported.

5.2. Uranium Series Disequilibrium Studies

Uranium series disequilibrium studies are a powerful tool for evaluating the preferential leaching of elements from uraninite. ^{238}U, with a half-life ($T_{½}$) of about 4½ billion years, has several radioactive daughters including ^{234}U ($T_{½}$ ≈ 2½ million years), ^{230}Th ($T_{½}$ = 77,000 years), ^{226}Ra ($T_{½}$ ≈ 1600 years), ^{222}Rn ($T_{½}$ ≈ 4 days), and ^{210}Pb ($T_{½}$ ≈ 22 years). Because ^{238}U has a half-life very much longer than any of its daughters, the abundance of ^{238}U remains the same for several half-lives of the daughter isotopes. Secular equilibrium may be established if there is no loss of daughter products, and, if this occurs, the rate of decay of the daughters becomes equal to that of the parent (Faure, 1986). If a decay series is in secular equilibrium, the activity ratios of the various radioactive nuclides (e.g. $^{226}Ra/^{238}U$) should be unity. Deviations from unity indicate loss of one nuclide with respect to the other. If uraninite dissolved incongruently we would expect to find activity ratios such as $^{226}Ra/^{238}U$ that were not equal to unity in the mineral and in the groundwater.

The present day groundwater chemistry from the Cigar Lake uranium ore deposit shows low total uranium concentrations, reflecting the reducing nature of the orebody environment. The groundwaters also show high radioactivities of radium and radon (analyses 79, 79, 91, 91A of Table A1.3). The radioactivities of Ra and Rn are higher than can be explained by the concentration of uranium present, and are evidence for disequilibrium in the uranium series. The disequilibrium is a product of preferential leaching of Ra and Rn from uraninite. It is unfortunate that activity ratios are not available for the uraninite at Cigar Lake. One must conclude, however, on the basis of the groundwater analyses that preferential leaching of Ra and Rn is occurring. This means that for Ra and Rn dissolution from uraninite is incongruent with respect to uranium at the Cigar Lake ore deposit.

Dickson and Snelling (1978) report activity ratios of $^{238}U/^{230}Th$ and $^{238}U/^{226}Ra$ from the Koongarra ore deposit. Samples were taken from different levels of the ore deposit, including the shallow weathered zone, the transitional zone, a fractured zone, and wall rock adjacent to the orebody. In general, most of the samples except those from the dispersion fan emanating from the weathered zone show enrichment of radium with respect to uranium. Dickson and Snelling (1978) interpret this to be the result of accumulation of radium that migrated from deeper unsampled regions of the orebody. If this is true, it would imply incongruent leaching of uranium at depth in what is suspected to be a slightly reducing environment. There are limitations on the use of this study to infer uraninite dissolution. This is because the activity ratios were determined on whole rock samples. The minerals present in the rock samples were largely secondary alteration products of uraninite. Thus, the use of radium accumulation in these samples to infer Ra loss from uraninite is ambiguous.

5.3. U-Pb Geochronology

Dating methods using the U-Pb system can be used to evaluate the solution mechanisms of uraninite. Among the more useful approaches in the U-Pb system is the U-Pb concordia diagram, which plots $^{206}Pb^*/^{238}U$ versus $^{207}Pb^*/^{235}U$ (the asterisk indicates radiogenic lead). If a uranium-bearing mineral has remained closed through geologic time, the Pb^*/U ratios would plot on a curve called 'concordia'. If uraninite lost lead at some point after initial crystallization, we would expect to find analyses of uraninites plotting off concordia, described as 'discordant.' The distribution of data points relative to concordia can often be used to infer the relative mobilities and timing of mobility of U and Pb in uraninite. Currently available U-Pb data for uraninite are typically discordant indicating Pb has been lost with respect to uranium at some stage of their history. The ore deposits listed below represent a range of redox conditions. The inference is that the

stability of uraninite does not prevent the loss of lead.

The discordancy and scatter in the data from Oklo (Gancarz, 1978) is suggestive of continuous lead loss by diffusion over 2000 million years. The average loss of lead from uraninite was estimated by Gancarz (1978) to be on the order of 50%. The U-Pb data for uraninites and sulphides at Jabiluka, are also highly discordant (Gulson and Mizon, 1980) but show a more complex history that is difficult to interpret.

The U-Pb data for Rabbit Lake (Cumming and Rimsaite, 1979) also indicate a complex history of Pb diffusion and losses. Cumming and Rimsaite (1979) give galena crystallization ages in an interval of 850 to 200 Ma ago. Episodes of uranium mobility was documented by Cumming and Rimsaite (1979) at ≈ 440 Ma (formation of uraniferous phyllosilicates), 200 Ma ago (formation of coffinite), and present day formation of hydrous uranyl-bearing minerals. Cumming and Rimsaite (1979) conclude that some processes such as Pb diffusion from pitchblende were long lasting, while remobilization of uranium and formation of sulphides was episodic.

The U-Pb data for Cigar Lake (Ruzicka and Lecheminant, 1986) consists of three collinear analyses whose discordia indicate a lead loss of about 30%. A lower intercept for the discordia of ≈ 200 Ma may correlate with the episode of Pb loss at Rabbit Lake described by Cumming and Rimsaite (1979), however the sparsity of data makes it difficult to interpret with certainty.

5.4. Fission Yields

This method is applicable to natural nuclear reactors such as Oklo at Gabon, Africa. The natural reactors at Oklo consist of well crystallized uraninite without evidence of hydrated uranium minerals indicating a long term reducing environment. The absence of ^{235}U enriched rims on the uraninites support an environment with low uranium solubility and transport (Duffy, 1978). Of the fission reactions that occur in natural uranium ore, neutron induced fission occurs primarily to ^{235}U (≈88%) and to a lesser degree to ^{239}Pu (≈8%) and ^{238}U (≈4%), such as demonstrated by Loss et al. (1988) for Reactor Zone 9 at Oklo. Calculations based on presumed immobile radionuclides (Pd in the case of Loss et al., 1988) have been used to predict the fission yields which are corrected for pre-fission abundances. The predicted isotopic abundances of radionuclides formed by fission can be used to detect preferential loss of radionuclides. Radionuclides that had been preferentially leached would have lower isotopic abundances than predicted.

Examples of loss of radionuclides by uraninite from Oklo have been reported by Cowan (1978). The nuclides that showed the largest loss (≈ 90% or more) were Pb, Nb, Zr, Ru, Ag, Te, Sr, Ba, Mo, Kr, Rb, Xe, and presumably Cs, Cd, and I. All of the elements cited except Cd have ionic radii (see Table 2) that are grossly incompatible with U^{4+}. This is strong evidence that the mobility of elements incompatible with the uraninite structure is not controlled by the solubility of uraninite, but by the crystal-chemical properties of the element in question.

5.5. Summary of Geological Evidence

The natural ore bodies considered in this report have all precipitated from relatively low temperature aqueous fluids. These fluids were probably oxidized brines that were modified chemically by mixing with reducing fluids or by interaction with country rocks of low oxidation potential (such as graphitic gneisses). They can be described as unconformity-type or stratabound sedimentary ore deposits. The host rocks were initially sandstones interbedded with shales. These ore deposits have experienced a range of redox environments since their initial deposition. They range from reducing environments of long duration (e.g. Cigar Lake and Oklo) to severe oxidizing environments caused by erosion and infiltration of surficial groundwaters (e.g. Koongarra and Rabbit Lake). Some have undergone low grade metamorphism, while others have not. The ore deposits of Oklo have experienced nuclear fission which has altered the temperature of the orebody during the fission process and resulted in the accumulation of fission products.

5.5.1 Rabbit Lake

Rabbit Lake is a uranium ore deposit which was initially created in a reducing environment, was subject to episodic remobiliztion of pitchblende, and more recently was subjected to severe weathering. The five generations of pitchblende record the early stages of the orebody's history. During these early stages the dissolution and precipitation of pitchblende was in the strict mineralogical sense "congruent". This description applies to the UO_2 dissolving and reprecipitating as UO_2. In other words, uranyl-bearing minerals were not formed by the reaction of pitchblende with the dissolving fluid. The description "congruent" does not necessarily apply to the trace elements. Pb in particular did not behave congruently during this stage. This is evidenced by the appearance of galena whose lead content included anomalously high radiogenic lead. Corroborating evidence is found in the discordant U-Pb ages documenting lead loss from pitchblende. The presence of excess radiogenic lead in galena and the depletion of lead in uraninite can only be interpreted to mean that lead behaved incongruently

with respect to uranium during this period. In the latter stages of Rabbit Lake's history, the pitchblende was oxidized and hydrated to form secondary alteration products. A reaction relationship with the fluid is evidenced by the replacement textures between the pitchblende and the alteration products. Since the stoichiometry of U and Pb of these secondary minerals is vastly different from uraninite, one can infer that U and Pb which enter the secondary mineral will probably not be in the same ratio as they were in pitchblende. The formation of reaction products with a fluid is in the strict mineralogical sense first hand evidence of incongruent dissolution with respect to the major elements. The geological evidence at Rabbit lake strongly suggests that the dissolution of pitchblende is incongruent, with regard to Pb and possibly other trace elements.

5.5.2 Cigar Lake

Cigar Lake hosts an extremely rich uranium ore deposit that is 400 m below the surface. The only indication of its presence in the groundwater is the anomalous radioactivity of both Ra and Rn. The low concentration of uranium is incapable of explaining the high radioactivities of Ra and Rn in the groundwater. It appears certain that the Ra and Rn are the result of preferential leaching from uraninite. The uraninite appears, however, to be stable based on the low concentration of uranium in the groundwater and on the lack of evidence for secondary alteration products of uraninite in drill cores from the orebody. Additional information on element mobility comes from the presence of galena with high abundances of radiogenic lead and from the U-Pb geochronology. The discordant ages reported by Ruzicka and Lecheminant (1986) and the existence of radiogenic galena indicate that, although uraninite was apparently stable, lead was preferentially leached. The evidence clearly shows that dissolution of Ra, Rn, and Pb was incongruent with respect to uranium at Cigar Lake.

5.5.3 Alligator Rivers

The Alligator Rivers uranium field hosts the Jabiluka and Koongarra ore deposits among others. The mineralogical evidence from Koongarra shows a reaction relationship between uraninite and the fluid. The preservation of a uraninite remnant being progressively replaced by hydrated U-Pb oxides is unequivocal evidence for incongruent dissolution in the strict mineralogical and thermodynamic sense. Although ambiguous, activity ratios of the uranium decay-series in the altered ore of Koongarra imply movement of Ra with respect to uranium. A U-Pb age for a Koongarra uraninite is described by Gulson and Mizon (1980) as being extremely discordant. U-Pb geochronology from the Jabiluka orebody (Gulson and Mizon, 1980) also yield discordant ages. The loss of lead at Jabiluka is

confirmed by the presence of excess radiogenic lead in sulphides (e.g. galena) associated with the uraninite. The evidence from Koongarra and Jabiluka is consistent with incongruent behaviour of certain trace elements.

5.5.4 Oklo

The natural reactors at Oklo have many of the trace elements that would be considered toxic radionuclides in spent fuel. The U-Pb ages reported by Gancarz (1978) were discordant. Gancarz (1978) interpreted the discordancy of the U-Pb ratios as symptomatic of continuous lead diffusion from uraninite. Cowan (1978) reported losses of Kr, Rb, and Xe of up to 99%, of Nb, Zr, Ru, Ag, Te, Sr, and Ba of up to 90%, and of up to 75% Pb from uraninite. This evidence clearly rules out the possibility of congruent behaviour for many trace elements in uraninite.

The evidence from U-Pb isotopes of uraninites from all deposits leads to the conclusion that Pb is leached preferentially from uraninite and does not behave congruently with respect to U. Radium when analyzed also appears to behave incongruently. The lack of quantitative isotopic analyses for trace elements (e.g. uranium daughter and fission products) in the majority of ore deposits hampers our ability to discuss the behaviour of elements other than Pb and Ra in different geochemical settings. Thus the data from Oklo is the only evidence available for quantitative assessment of the mobility of elements other than Pb and Ra. The available data imply that many elements are released preferentially from uraninite.

6. CONCLUSIONS AND RECOMMENDATIONS

The focus of this report has been on evaluating the validity of modelling spent fuel stability based on an assumption of congruent dissolution of uraninite. Data have been compiled and assessed on the evidence that natural uranium ore deposits provide on the relative mobility of the elemental constituents of uraninite. The questions that were addressed in this report are:

1. Is it valid to model the dissolution of fuel rods by the dissolution of uraninite (the major uranium bearing mineral in natural ore bodies)?

2. Are the radiogenic and fission produced elements that result from radioactive decay and fission processes preferentially leached from uraninite?

3. What is the effect of groundwater chemistry on the mechanism of uraninite dissolution?

The major conclusions of the study are as follows:

1. The presence of unannealed radiation damage to spent fuel rods may affect the validity of using dissolution studies of unirradiated uraninite as analogues for spent fuel dissolution. Theoretical evaluation of uraninite dissolution indicates that in general it is not valid to model the release of trace elements, some of which may be toxic, from uraninite as if they were controlled by the dissolution of UO_2. This occurs because trace elements may act as independent components whose solubilities in fluids are independent of that of uraninite. Nevertheless, elements which have very similar electronic properties as U (Th, Am, Ce^{4+}, Cm, Np, Pa, Pu) can probably be modelled as if they had similar behaviour as U, but this would have to be verified by empirical observation. The release of trace elements that are not contained in the crystallographic sites of uraninite, or that are contained within exsolution phases in uraninite, should not be modelled as if they were dependent on uranium oxide solubility. Such elements include Ag, Ba, Cs, I, Mo, Nb, Pb^{2+}, Ra, Rb, Rh, Ru, Sr, Sn, Tc, Te, and Tl^{1+}.

2. The evidence from natural ore bodies is consistent with the theoretical evaluation, and indicates that trace components of natural uraninite are often preferentially released relative to uranium oxide undergoing both congruent or incongruent (reaction) dissolution. The major evidence for preferential mobility of trace elements is provided by the common presence of radiogenic galena in otherwise stable uraninite ore

deposits, the ubiquitous discordant U-Pb ages for uraninite, the presence of disequilibrium in the U decay series, and the mismatch of observed isotope abundances and those calculated from fission yields in the Oklo natural reactor.

3a. The dissolution mechanism of UO_2 is dependent on the groundwater chemistry, in particular its redox potential. Under reducing conditions, where uraninite is stable the release of trace elements is a function of the relative partitioning of the element between uraninite and the fluid, the rate of transfer of elements to the crystal/fluid interface, the rate at which elements are exchanged with the fluid (i.e. surface reactions), and the rate of element transfer away from the crystal. Evidence from the Oklo natural reactor indicates that the rate limiting process is the rate of surface reactions rather than the rate of diffusion through the bulk crystal.

3b. Under oxidizing conditions, the chemistry of the groundwater will determine whether dissolution of uraninite is congruent or incongruent. If the groundwater contains dissolved phosphates or silicates, uraninite may dissolve incongruently by reaction with the fluid, forming uranyl phosphates or uranyl silicates. The release of trace elements during this process is unlikely to be correlated with uranium oxide, except for those elements with similar electronic properties.

In order to confidently model the release of trace components, it would be desirable to know: (a) the trace element abundances in uraninite (or spent fuel) and fluid; (b) the partition coefficient for the trace element between uraninite, reaction products, and the fluid; (c) the diffusion rate of the trace element in uraninite; (d) the rate of element transfer at the fluid/uraninite interface; (e) the fluid/uraninite mass ratio.

TABLE 1: URANINITE AND PITCHBLENDE ANALYSES (Wt%)						
	1	2	3	4	5	6
CaO	0.08	0.11	0.18	0.84	0.37	1.00
MnO	-	-	0.10	0.16	-	0.09
PbO	3.14	3.08	4.35	0.70	9.04	6.39
MgO	-	-	-	-	-	0.17
$(Y,Er)_2O_3$	-	-	-	-	1.11	.nd
$(Ce,La)_2O_3$	9.57	11.10	-	-	-	-
La_2O_3	-	-	-	-	0.27	.nd
Ce_2O_3	-	-	-	0.22	0.18	.nd
UO_2	59.13	59.93	72.25	58.51	46.13	59.30
UO_3	22.08	23.03	13.27	25.26	30.63	22.33
ThO_2	-	-	7.20	-	6.00	.nd
ZrO_2	-	-		7.59	0.06	-
SiO_2	1.06	0.16	0.03	2.79	0.22	0.50
Al_2O_3	-	-	-	-	-	0.20
Fe_2O_3	1.21	0.29	0.11	-	0.25	0.21
H_2O	0.97	0.43	0.68	1.96	0.74	3.17
Insoluble	0.85	0.89	0.04	-	4.42	-
Remainder	0.96	2.47	-	1.92	1.19	4.59
Total	99.05	101.49	98.21	99.95	100.61	97.95
Sp gr	9.139	9.622	9.733	8.068	8.893	6.89

1. Uraninite. Crystal from pegmatite. Hale's quarry, Glastonbury, Conn. Average of two analyses. Analyst Hillebrand, *in* Frondel (1958). Remainder is Nb_2O_5. (The correct locality is Strickland's quarry, Portland, Conn.)
2. Uraninite. As above but different specimen. Analyst Hillebrand, *in* Frondel (1958). Remainder is He 2.41, P_2O_5 0.02, F 0.04.
3. Uraninite. Pure lustrous crystal from pegmatite. Branchville, Conn. Analyst Hillebrand, *in* Frondel (1958).
4. Pitchblende. Vein deposit near Black Hawk, Gilpin County, Colo. Analyst Hillebrand, in Frondel (1958). Contains admixed sulfides; average of 2 analyses. Remainder is ZnO 0.44, FeO 0.32, He 0.15, P_2O_5 0.22, As_2O_5 0.43, $CuFeS_2$ 0.12, FeS_2 0.24.
5. Uraninite (brŏggerite). Crystal from pegmatite. Gustavagruben, Annerŏd, Norway. Analyst Hillebrand, *in* Frondel (1958). Remainder is He 1.17, P_2O_5 0.02.
6. Pitchblende. Johanngeorgenstadt, Saxony. Analyst Hillebrand, *in* Frondel (1958). Remainder is He 0.02, Na_2O 0.31, Bi_2O_3 0.75, CuO 0.17, P_2O_5 0.06, As_2O_5 2.43, (V, W, Mo) oxide 0.75, SO_3 0.19.

TABLE 2: IONIC RADII OF SOME RADIONUCLIDES

nuclides	oxidation state	ionic radii (Å)	% change
Ag	1^+	1.38	27.78
Am	4^+	1.03	-4.63
Ba	2^+	1.50	38.89
Bi	3^+	1.19	10.19
Cd	2^+	1.15	6.48
Ce	3^+	1.22	12.96
	4^+	1.05	-2.78
Cs	1^+	1.82	68.52
Cm	4^+	1.03	-4.63
Hg	2^+	1.22	12.96
In	3^+	1.00	-7.41
La	3^+	1.26	16.67
*Mo	3^+	0.75	-30.56
	6^+	0.68	-37.04
*Nb	5^+	0.72	-33.33
Nd	3^+	1.20	11.11
Np	4^+	1.06	-1.85
Pa	4^+	1.09	0.93
Pb	2^+	1.37	26.85
	4^+	1.02	-5.56
Po	4^+	1.16	7.41
Pr	3^+	1.08	0
	4^+	1.07	-0.93
Pu	4^+	1.04	-3.70
Ra	2^+	1.56	44.44
Rb	1^+	1.68	55.56
Rh	3^+	0.75	-30.56
	4^+	0.71	-34.26
*Ru	3^+	0.76	-29.63
	4^+	0.70	-35.18
Sr	2^+	1.33	23.15
Sn	2^+	1.30	20.37
Sm	3^+	1.17	8.33
*Tc	4^+	0.72	-33.33
*Te	4^+	0.60	-44.44
Th	4^+	1.12	3.70
Tl	1^+	1.68	55.56
	3^+	1.08	0
U	4^+	1.08	0
Y	3^+	1.10	1.85
Zr	4^+	0.92	-14.81

coordination number (CN) = VIII, except for nuclides indicated by an "*" then CN = VI for Ru, Mo, Tc, and Nb, and CN = III for Te
Sources: Jeffery (1967), Faure (1988), Krauskopf (1988), Whittaker and Muntus (1970)

TABLE 3: URANIUM MINERALIZATION AND ASSOCIATIONS

PRIMARY MINERALS:

brannerite	$(U, Ca, Ce)(Ti, Fe)_2O_6$
coffinite	$USiO_4$
davidite	$(Fe^{2+}, La, U, Ca)6(Ti,Fe^{3+})_{15}(0, OH)_{36}$
pitchblende	UO_2 essentially no Th, REE
uraninite	UO_2 with Th, REE
uranothorite	$(Th, U)O_2$

SECONDARY MINERALS:

becquerelite	$CaU_6O_{19}\cdot 11H_2O$
boltwoodite	$K_2(UO_2)_2(SiO_3)_2(OH)_2\cdot 5H_2O$
carnotite	$K_2(UO_2)(VO_4)_2\cdot 1\text{-}3H_2O$
coffinite	$U(SiO_4)_{1-X}(OH)_{4X}$
curite	$2PbO\cdot 5UO_3\cdot 4H_2O$
dewindite	$Pb(UO_2)_4(PO_4)_2\cdot 3H_2O$
fourmarierite	$PbO\cdot 4UO_3\cdot 4H_2O$
johannite	$Cu(UO_2)_2(SO_4)_2\cdot 6H_2O$
kasolite	$Pb(UO_2)SiO_4\cdot H_2O$
masuyite	hydrated Pb-U oxide
renardite	$Pb(UO_2)_4(PO_4)_2(OH)_4\cdot 7H_2O$
saleeite	$(UO_2)_2(PO_4)_2\cdot 8H_2O$
sklodowskite	$Mg(UO_2)_2Si_2O_7\cdot 6H_2O$
sabugalite	$HAl(UO_2)(PO_4)_4\cdot 16H_2O$
thucolite	hydrocarbon with U, etc.
torbernite	$Cu(UO_2)_2(PO_4)_2\cdot 8\text{-}12H_2O$
tyuyamunite	$Ca(UO_2)(VO_4)_2\cdot 5\text{-}8H_2O$
uranophane	$Ca(UO_2)_2Si_2O_7\cdot 6H_2O$
vandendriesscheite	$PbU_7O_{22}\cdot 12H_2O$
wölsendorfite	$(Pb,Ca)U_2O_7\cdot 2H_2O$
zippeite	$K_2(UO_2)_2(SO_4)_3(OH)_{10}\cdot 4H_2O$

ACCESSORY MINERALS:

allanite	$(Ce, Ca, Fe^{2+}, Y, U, Th)_2(Al, Fe^{3+})_3(SiO4)_3(OH)$
apatite	$(Ca, REE)_5(PO_4, CO_3, OH)_3(F, Cl, OH)$
monazite	$(Ce, La, Nd, Th)PO_4$
sphene	(Ca, Na, REE, Mn, Sr, Ba) $(Ti, Al, Fe^{3+}, Mg, Nb, Ta, V, Cr)(SiO_4)(O, OH, F)$
zircon	$(Zr, U, Th, Hf)SiO_4$

TABLE 3 (CONTINUED): URANIUM MINERALIZATION AND ASSOCIATIONS

METALLIC ASSOCIATIONS:

		Sulphides	
bravoite	$(Ni,Co,Fe)S_2$	greenockite	CdS
bornite	Cu_5FeS_4	jordisite	MoS_2
chalcocite	Cu_2S	marcasite	FeS_2
chalcopyrite	$CuFeS_2$	molybdenite	MoS_2
covellite	CuS	pyrite	FeS_2
digenite	Cu_9S_5	smythite	$(Fe,Ni)_9S_{11}$
galena	PbS	sphalerite	ZnS
		sulpharsenides	
cobaltite	$CoAsS$	gersdorffite	$NiAsS$
glaucodot	$(Co,Fe)AsS$		
		arsenides	
niccolite	$NiAs$	skutterudite	$(Co, Ni)As_3$
smaltite	$(Co,Ni)As_{3-X}$	rammelsbergite	$NiAs_2$
		selenides, tellurides	
Altaite	$PbTe$	clausthalite	$PbSe$

GANGUE:

anatase/rutile	TiO_2	goethite	$FeO{\cdot}OH$
barite	$BaSO_4$	gypsum	$CaSO_4{\cdot}2H_2O$
Calcite	$CaCO_3$	hematite	Fe_2O_3
dolomite	$CaMg(CO_3)_2$	limonite	$FeO{\cdot}OH{\cdot}$
fluorite	CaF_2	quartz	SiO_2
kaolinite	$Al_4(Si_4O_{10})(OH)_8$		

Sources:
Deer, Howie,and Zussman (1977)
Hurlbut and Klein (1977)
Frondel (1958)
Stanton (1972)
Steacy and Kaiman (1978)

TABLE 4: MICROPROBE ANALYSES (WT%) OF SPENT FUEL				
	1	2	3	UO_2 matrix
Rh	5	minor	nd	-
Ru	18	9	nd	-
Te	13	6	nd	-
Mo	41	21	minor	-
Zr	nd	10	10	0.5
Ce	nd	6	5	0.6
Ba	nd	20	25	-
U	12-20	16-30	25-50	-
La	-	-	-	0.5
Pr	-	-	-	0.4
Nd	minor	minor	minor	0.7
Pd	minor	-	-	-
Sr	-	minor	minor	-

from Jeffery (1967)
1,2, & 3 were exsolved inclusions within the UO_2 matrix
"-" indicates no analysis
"nd" indicates not detected

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APPENDIX A: DESCRIPTION OF URANIUM ORE DEPOSITS

Natural analogues to deep burial of radioactive waste have been investigated by numerous workers as a means to bridge the temporal gap between experiments that are necessarily short (a fraction of man's lifetime) and the requirements of a disposal program (several half-lives of the more toxic radionuclides). The nuclides produced by fission have relatively short half-lives and will have lost most of their radioactivity after approximately 600 years. The transuranic nuclides have much longer half-lives. It would take several million years for these nuclides will decay to activities that are characteristic of natural uranium ore deposits (Aikin et al., 1977). The following sections summarize some of the more intensely studied natural uranium ore bodies, the ore deposits of the Athabasca Basin, the Pine Creek Geosyncline, and the natural reactor of Oklo. They are all of the unconformity-type or stratabound in nature and proterozoic in age. The differences are in the grade of ore, occurrence or absence of fission, and their geochemical environment with its affect on mineral and nuclide stability.

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A1. Uranium Ore deposits of the Athabasca Basin

The Athabasca basin of northern Saskatchewan is host to numerous uranium deposits. An overview of the geology of northern Saskatchewan is documented in Hoeve and Sibbald (1978), and Sibbald (1986, 1988). The ore deposits are associated with the unconformity between the crystalline basement rocks and the overlying Athabasca group of fluvial and marine clastic sedimentary rocks. The unconformity is a paleoweathered surface similar to that of present day laterites. The unconformity-type uranium deposits are concentrated along the eastern margin of the basin and in the Carswell structure located centrally in the west. The main characteristics of the deposits as summarized by Sibbald (1987) are:

1) proximity to the unconformity;
2) association with the graphitic basement rocks;
3) structurally controlled by faults, topographic highs, and collapse structures;
4) alteration halos, typified by illitization, Mg-chloritization, Mg-tourmalinization, silicification, dolomitization, and

hematization;
5) high grade uranium mineralization;
6) pitchblende and coffinite as primary uranium minerals;
7) mineralization (≈1300 Ma) postdates deposition of the Athabasca group (≈1450 Ma); and
8) the deposits typically show complex mineralogy and geochemistry.

The deposits in order of discovery (Sibbald, 1988) are: Rabbit Lake; Collins Bay (A, B, & D); Raven; Horseshoe; Fond-du-Lac; Eagle Point (North and South zone); Midwest Lake; Dawn Lake (11, 11A, 11B, & 14 zones); McClean Lake (North and South zones); Jeb; Key Lake; Cigar Lake; Maurice Bay; Cluff Lake (D and other); Carswell structure (Claude, Dominique-Peter, OP, N, Donna showing, and Sophie showing); and Westbear. Hoeve and Sibbald (1978) describe the genesis of the Athabasca unconformity-type deposits as being of diagenetic/hydrothermal origin. They envision oxygenated diagenetic fluids flushing the basin wide sandstones, dissolving and carrying uranium in solution. The diagenetic fluids have been described as heated brines, with temperatures in the range of 150-225°C, pressures from 0.7-1.5 kbar, and salinity on the order of 30 equivalent wt% NaCl (Pagel and Jaffrezic, 1977; Pagel et al., 1980). These oxygenated brines mixed with reducing fluids which emanated from the fractured basement, notably in areas associated with graphitic assemblages. The change in chemistry of the ore-bearing fluid resulted in the precipitation of uranium. This model assumes preconcentration of uranium and other metals in the sandstone beds. It does not address the question of primary origin of the uranium. An alternative model advocated by Dahlkamp (1978) invokes uranium concentration in the older lagoonal sediments that were metamorphosed and weathered prior to deposition of the Athabascan sandstones. Diagenetic processes then remobilized and redeposited the uranium.

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A1.1 Rabbit Lake:

The Rabbit Lake deposit is on the eastern margin of the Athabasca basin, west of Wollaston Lake. The Athabasca formation is absent due to glacial erosion, with evidence for mineralization present in boulder train. The minerals identified by Rimsaite (1977, 1978) include:

uranium and U-Pb oxides: pitchblende of five varieties and several generations; triuranium heptaoxides, Pb-bearing, masuyite-becquerelite, vandendriesscheite, and wöelsendorfite;
uranium-bearing silicates: coffinite, kasolite, uranophane, sklodowskite, boltwoodite, yttrialite, and allophane;
sulphides, selenides, and arsenides: galena, clausthalite, sphalerite, pyrite, chalcopyrite, bornite, chalcocite, covellite, nickeline, and carrollite;
phosphates: apatite and monazite;
sulphates: anhydrite, gypsum, zippeite, and barite;
oxides: quartz, hematite, goethite, rutile, and anatase; and
oxygenated hydrocarbons: thucholite.

Rimsaite (1978) distinguishes between the five varieties or generations of pitchblende on the basis of texture and Pb/U ratios. The five

generations of pitchblende (P-1 to P-5) show decreasing abundances of Pb with respect to uranium. Rimsaite (1977) attributes the characteristic Pb/U ratios of the five types of pitchblende to lead loss caused by migration and/or recrystallization. Also, different times of crystallization would affect the accumulations of radiogenic lead. Pitchblende type P-3 is described as recrystallized euhedral "urania" (tetragonal uraninite). This type of pitchblende was also recognized at Key Lake by Dahlkamp (1978). Type P-4 is associated with coffinite, chalcopyrite, bornite, covellite, and Co-Ni sulphides. The depletion of lead in P-4 pitchblende is interpreted to have resulted from lead migration (Rimsaite, 1978). The lead reacted with sulphide to form radiogenic galena. Rimsaite (1978) inferred from the mineralogy several episodes of remobilization and recrystallization of uranium. For the Rabbit Lake deposit sulphide-arsenide mineralization was an important event that caused remobilization of pitchblende with subsequent lead loss (Rimsaite, 1977, 1978). A separate thermal event was also inferred from the presence of recrystallized eastonite and sericite-like minerals surrounding the deposit. Supporting evidence for a thermal event was the dehydration of amorphous uranyl-bearing aggregates (Rimsaite, 1978).

TABLE A1.1: URANINITE AND PITCHBLENDE ANALYSES (WT%) RABBIT LAKE

	1	2	3	4	5	6	7
CaO	1.3	1.1	2.8	6.0	0.6	5.9	6.2
PbO	11.7	18.6	13.6	1.0	4.8	0.1	0.2
UO_2	85.1	51.5	61.6	78.8	81.9	77.3	68.2
SiO_2	0.1	3.6	3.2	3.2	0.0	9.9	12.4
FeO	0.1	0.0	0.0	0.0	0.0	0.0	0.0
TiO_2	0.3	0.0	0.0	0.0	0.0	0.0	0.0
UO_2/PbO	7.3	2.8	4.5	78.8	17	700	341
Total	98.6	74.8	81.2	89.0	87.3	93.3	79.8
Rem.	1.4	25.2	18.8	11.0	12.7	6.7	20.2

1. Massive, fractured pitchblende (P-1). Analysts: M. Bonardi, G. R. Lachance and A. G. Plant, *in* Rimsaite (1977).
2. Resorbed pitchblende (P-1), from brecciated ore. Analysts: M. Bonardi, G. R. Lachance and A. G. Plant, *in* Rimsaite (1977).
3. Resorbed pitchblende (P-2), from brecciated ore. Analysts: M. Bonardi, G. R. Lachance and A. G. Plant, *in* Rimsaite (1977).
4. Pb-depleted pitchblende (P-2), from brecciated ore. Analysts: M.

Bonardi, G. R. Lachance and A. G. Plant, *in* Rimsaite (1977).
5. Rectangular recrystallized pitchblende (P-3) in phyllosilicate groundmass. Analysts: M. Bonardi, G. R. Lachance and A. G. Plant, *in* Rimsaite (1977).
6. Impure pitchblende (P-4) recrystallized with fine grained Fe, Cu, Co, Ni-sulphides, coffinite, and carbonate. Analysts: M. Bonardi, G. R. Lachance and A. G. Plant, *in* Rimsaite (1977).
7. Uranophane filling fractures in brecciated ore. Analysts: M. Bonardi, G. R. Lachance and A. G. Plant, *in* Rimsaite (1977).

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A1.2 Cigar Lake

The deposits that are the subject of research by the Atomic Energy of Canada Limited (AECL) for the Canadian Nuclear Fuel Waste Management Program (CNFWMP) are Dawn, Key, and Cigar Lakes (Cramer, 1986a & b). Dawn Lake is located 30 to 200 metres beneath the surface; Key Lake 50 to 150 metres; and Cigar Lake is on the order of 400 metres beneath the surface. Dawn and Cigar Lake both lack surface indicators of their mineralization. Cigar Lake possesses a high grade ore (average of 12% and up to 65% locally) of large extent. The geology and mineralogy of Cigar Lake is documented in Bruneton (1986) and Fouques et al. (1986). Three types of mineralization are identified by Bruneton (1986) as:

1) main mineralization at the unconformity,
2) perched mineralization, and
3) basement mineralization.

The main mineralization is described as being of hydrothermal origin

and similar to other Athabasca deposits in its mineral paragenesis. Bruneton (1986) divides the main mineralization into the following stages:

uranium oxide: euhedral uraninite and pitchblende (radiating) associated with arsenides (rammelsbergite, niccolite, gersdorffite, cobaltite, and glaucodot) and sulphides (pyrite, marcasite, and bravoite), at ≈ 1300 Ma;
pitchblende facies: with secondary arsenides, sulpharsenides, sulphides (pyrite, marcasite, bravoite, smythite, chalcopyrite, digenite, chalcocite, covellite, galena, sphalerite, jordisite, and clausthalite); and
pitchblende-coffinite: with iron oxides and hydroxides, between 450 to 200 Ma ago.

The perched mineralization occurs in localized fracture within the sandstone above the main ore body. Although not common, significant accumulations of mineralization are known. The mineralogy consists of pitchblende-coffinite associations (of low ore-grade) with pyrite, marcasite, local bravoite, galena and microscopic hydrocarbons. The geochemistry suggests mobility of uranium with respect to other elements such as Ni, Co, Cu, Pb, As, and S. Bruneton (1986) interprets the "perched mineralizations" as indicating possible remobilization of uranium similar to what is described as "rabbit ears" at McClean Lake. The clay rich layer enveloping the Cigar Lake ore body is described by Percival (1989). It is comprised of four zones (from the ore body outwards):

1) Fe-chlorite + illite ± carbonate ± uraninite ± gersdorffite;
2) sudoite + illite ± hematite ± sulphides;
3) Illite + hematite; and
4) illite ± kaolinite ± hematite.

The illites grade from mixes of $3\underline{T}$-$2\underline{M}_1$ polytypes close to the ores to $2\underline{M}_1$-$1\underline{M}$ polytypes more distant from the uranium mineralization. Uranium extraction experiments on the altered clay halo from Cigar Lake (Percival, 1989) suggest that the uranium is largely bound in uraninite, residual silicates, and crystalline Fe-oxides. Percival (1989) interprets these results to indicate that the uranium was dispersed primarily by initial ore-forming fluids, not by secondary alteration processes. The present day

groundwaters are documented in Cramer (1986c). The waters in the ore zone appear to be characterized by neutral pH, low salinity (from measured conductivities), and of a reducing nature (see analyses 79, 79b, 91, 91a in Table A1.2).

TABLE A1.2: GROUNDWATER ANALYSES FROM CIGAR LAKE

Site	79	79B	91	91A	137
U (μg/l)	2.5	6.1	11.9	4.3	11.9
Ra (Bq/l)	17.39	1.44	2.49	2.72	3.16
Rn (Bq/l)	73608	868	474	1386	49
HCO_3 (mg/l)	131	116	112	102	114
HPO_4 (mg/l)	2.5	0.5	1.0	0.4	0.8
SO_4 (mg/l)	<0.1	1.2	5.8	7.0	0.5
CO_2 (cm^3/l)	11.791	12.620	7.980	8.543	1.788
Fe^{2+} (mg/l)	4.22	0.33	0.1	2.03	2.47
pH	7.14	7.09	7.08	7.35	7.32
Cond. (mS/cm)	.371	.334	.404	.293	.243
TDS* (mg/l)	260	234	283	205	170

#79, 79B, 91, & 91A, piezometer holes from ore zone.

#137 & 83B, artesian holes

Source: Cramer (1986c)

*calculated: 1mS/cm (conductivity) ≈ 700 mg/L (TDS)

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A2. Uranium ore deposits in the Northern Territory, Australia

A review of the geology of the Pine Creek Geosyncline in the Northwest Territory of Australia is given by Needham et al. (1980, 1988) and Langford (1978). The uranium deposits are unconformity-type and largely found in three areas; the Rum Jungle uranium field, the Alligator Rivers uranium field, and the South Alligator Valley uranium field. The geology of the Koongarra, Jabiluka, Nabarlek, and Ranger ore deposits of the Alligator Rivers uranium field are further described by Needham and Stuart-Smith (1980). The basement rocks consist of Archean to Lower Proterozoic Granitoids, overlain by the Kakadu Group of metasediments. The meta-arkose, leucocratic gneiss, and quartzite of the Kakadu group are characterized by preserved bedding and compositional banding. They are possibly the oldest Lower Proterozoic metasediments in the Pine Creek geosyncline (Needham and Stuart-Smith, 1980). The Cahill formation overlies the Kakadu group and is composed of carbonate and carbonaceous rocks (lower member) grading upwards into the more psammitic upper member. The Cahill formation experienced regional metamorphism to an amphibolite grade at around 1800 Ma.

The uranium deposits in the Alligator Rivers region are hosted by the lower member of the Cahill formation. The lower member is a quartz-muscovite-chlorite schist with some carbonaceous, pyritic, and garnetiferous components (Langford, 1978; Needham and Stuart-Smith, 1980). The mainly graphitic, carbonaceous material, while ubiquitous, is not believed by Ewers and Ferguson (1980) to be related to the uranium mineralization. The degree of chloritization appears to be strongly correlated with uranium mineralization. The ores tend to be located in brecciated zones. Ewers and Ferguson (1980) interpret the textures and lithology of the brecciation as being younger than the regional metamorphism, with the breccia fragments cemented by chlorite ± quartz ± hematite ± chert ± graphite ± sulphides ± uraninite. Uraninite is the primary uranium bearing mineral in each deposit with minor brannerite, coffinite, and rare thucolite. Ewers and Ferguson (1980) interpret the textures of the uraninite to indicate remobilization and redeposition of the uranium. The textures include disseminated uraninite coalescing into strings, clusters, narrow lenses, massive uraninite, and veining of foliation planes, and hairline fractures which appear to postdate mineralization and are discordant to the foliation planes. Lead isotope studies at Jabiluka (Gulson and Mizon, 1980) give young apparent ages that are likely the result of lead loss from diffusion and/or leaching of radiogenic lead. Sulphides associated with uranium mineralization contain excess radiogenic lead.

The lack of strong evidence for a correlation between mineralization and graphite has led to conflicting models of ore genesis. Ewers and Ferguson (1980) suggest concentration of uranium from an oxidized solution by adsorption onto clay minerals. They postulate reduction of the uranyl complexes after adsorption by redox reactions with the oxidation of Fe^{2+} to Fe^{3+} as the other half-reaction. Alternatively, Gulson and Mizon (1980) explain the lack of correlation between mineralization and a reducing environment by proposing that uranium was transported in brines rather than Co_2-rich fluids as the U(IV) species negating the need for reducing agents. However, the conventional model of epigenetic hydrothermal deposition controlled in part by redox reactions between the uranium bearing aqueous fluids and graphitic schists is preferred by Binns et al. (1980b). The nature of the ore forming fluids has been constrained by fluid inclusion and oxygen isotope studies on the Nabarlek ore deposit (Ypma and Fuzikawa, 1980). Three distinct fluids were identified: late metamorphic brines characterized by NaCl and high density CO_2-rich inclusions, with homogenization temperatures estimated to be in excess of 350°C; concentrated brines of $CaCl_2$, $MgCl_2$, and NaCl with large spatial extent and homogenization temperatures between 110° and 160°C; and CO_2-rich brines that appear to be confined to the ore zone and contain vapour rich

inclusions (of up to 45 wt% CH_4) . Ypma and Fuzikawa (1980) propose that uranium deposition occurred from the mixing of a hypersaline brine with a CO_2-rich fluid of meteoric origin. Present day groundwaters near the Jabiluka ore deposit (Deutscher et al.,1980) are given in Table A2. In general, they are characterized by low salinity, neutral to slightly acidic pH, and slightly reducing to slightly oxidizing.

The Koongarra ore deposit is of interest due to the formation of secondary uranium mineralization. Snelling (1980) describes and interprets the formation and pattern of the secondary uranium-lead oxides and uranyl silicates, that are found at depth in the ore zone of the No. 1 orebody, and the uranyl phosphates, which are located in the weathered upper zone and dispersion fan above the ore body. The primary mineralization is uraninite characterized by low to negligible thorium contents and REE's, two groupings of calcium content (one between 1 and 2%, the other between 3 and 5%), and variable lead contents indicative of lead loss. The first type of pitchblende (1-2% Ca) is thought to have formed during initial deposition of the vein-type ores under moderate temperatures, their morphology is crystalline with subhedral grains. Pitchblendes of the second type, with higher calcium content, are more oxidized. Their morphology (colloform banding) is characteristic of low temperature, supergene precipitation. Snelling (1980) interprets the high calcium pitchblendes as the result of a second period of uranium remobilization.

The secondary oxides are curite, fourmarierite, and vandendriesscheite. The silicates are kasolite, sklodowskite-uranophane. The phosphates are saleeite, sabugalite, torbernite, and renardite-dewindtite. Also identified is the sulfate johannite and the vanadate carnotite-tyuyamunite. A combined electron microprobe-scanning electron microscope study of the alteration products showed incomplete redistribution of magnesium, calcium, silicon, lead, and uranium (Snelling, 1980). This evidence and the presence of primary uraninite remnants suggest that there was insufficient time for equilibration, indicating that the alteration was recent with respect to ore formation, and confirms the in situ nature of the alteration process.

Dickson and Snelling (1980) investigated the uranium series disequilibrium at the Koongarra deposit to determine the movement of uranium and its daughter products. They found equilibrium ratios for ^{230}Th and ^{226}Ra, but disequilibrium between ^{230}Th and ^{238}U in the samples from the upper weathered zone indicative of uranium mobility in that region. In the transitional zone samples showed enrichment of ^{226}Ra relative to ^{238}U and depletion of ^{230}Th suggestive of Ra deposition and possible loss of

uranium. A sample from the ore zone showed equilibrium between ^{230}Th and ^{238}U. There was a considerable enrichment of Ra relative to U in the ore zone sample, which Dickson and Snelling (1980) interpret as evidence for radium mobility at depth.

They suggest that the geochemistry of circulating waters in the shallow environment was different from that of the ore zone. The mineralogy of the ore zone reflects a more reducing groundwater with slightly acidic pH, high silica content, and very low dissolved phosphate. This chemistry would favor the stability of uraninite and uranyl silicates over uranyl phosphates. The reducing environment would also favor mobility of radium (Snelling, 1980; Dickson and Snelling, 1980). In the upper zone, the Eh would be slightly higher and the weathering of apatite (common in the host schists) would increase the total phosphate concentration in the groundwater. These conditions would favor the stability of uranyl phosphates. Dickson and Snelling (1980) and Snelling (1980) concluded that the alteration of the primary pitchblendes occurred in the following sequence:

1) slightly oxidizing, low temperature groundwaters produced new chlorite growth and alteration of uraninites to uranium-lead hydrous oxides and uranyl silicates, with migration and redeposition of uraninites;
2) further erosion led to oxidizing, surficial weathering which produced uranyl phosphates from the weathered and leached uraninites and uranyl silicates;
3) lateral movement of groundwater in the weathered zone led to the prominent dispersion of the secondary mineralization above the ore body; and
4) the alteration processes, which occurred in situ, were relatively recent and slow.

Table A2 Groundwater Analyses Jabiluka #1 & #2 Ore Bodies					
	l.d.	224	225	421	420
Ca^{2+} (mg/l)	1	1	1	1	3
Mg^{2+} (mg/l)	1	19	9	1	7
Na^{+} (mg/l)	1	2	1	5	5
K^{+} (mg/l)	1	1	1	2	2
Si(mg/l)	1	7	7	15	12
$SO_4^{=}$ (mg/l)	5	13	nd	44	14
Cl^{-}(mg/l)	5	9	6	22	20
HCO_3^{-} (mg/l)	5	185	71	12	73
F^{-}(mg/l)	2	-	-	0.2	0.2
Fe^{2+} (mg/l)	0.1	4	nd	nd	nd
Zn(μg/l)	5	5	13	nd	nd
Cd (μg/l)	3	nd	nd	nd	nd
Pb (μg/l)	5	nd	nd	nd	nd
Cu (μg/l)	5	nd	nd	nd	nd
U (μg/l)	1	1	1	1	9
pH		7.20	7.55	6.00	6.05
Eh (Volts)		0.06 to 0.15			
cond (mS/cm)		.620 to .680			
TDS(1mS/cm ≈ 700 mg/l)		≈450			

"l.d." indicates limit of detection
Source: Deutscher et al. (1980)

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A3. The Oklo Natural Reactor

The anomalous ^{235}U abundance of the uranium orebodies at Oklo in Gabon, Africa was presented to the scientific community by H. Bouzigues, R. J. M. Boyer, C. Seyve and P. Teulieres in 1972 (see Bouzigues et al., 1975). The depletion of ^{235}U (0.7171 at% as opposed to 0.7202 at%) led the French scientists at the Pierrelatte Diffusion Plant to conclude that a natural self-sustaining nuclear reactor had been discovered. The announcement was followed by a symposium in Libreville with a collection of 40 papers published in the volume, *The Oklo Phenomenon* (1975). A second symposium was held in Paris, with 39 papers published in the volume, *Natural Fission Reactors* (1978). A review of the literature on the geology and geochemistry of the Oklo reactors is given by Jakubick (1986).

Gauthier-Lafaye and Weber (1989) describe the geology and geochemistry of the Franceville basin (Gabon). The Franceville basin contains a metamorphosed series, the Ogooué mobile zone, and the unmetamorphosed sediments of the Francevillian series. The Francevillian series has been divided by Gauthier-Lafaye and Weber (1989) into five separate formations. The FA formation at the base of the series contains the uranium mineralization. This formation is characterized by a marine transgression of deltaic sediments overlying fluviatile deposits. The FA formation is itself overlain by impermeable black shales of the FB formation. The uranium ore deposits in the FA formation are located in the transitional sediments between the fluviatile and prodeltaic depositional sequences and are associated with tectonic structures. Gauthier-Lafaye and Weber (1989) suggest that sedimentation, burial, and uplift had the following effects on the uranium mineralization:

Sedimentation: this occurred around 2100 Ma, with the deposition of radioactive fluviatile conglomerates, containing thorite and uraniferous thorite (the source of the uranium mineralization), and sandstones. This was followed by deltaic and marine deposits;

Burial: remobilization of uranium by oxidizing connate fluids, with the depth of burial as 4 km and temperature around 180°C;

Uplift: temperature decreasing to 140°C and an uplift of 1 km. Associated with uplift was hydrofracturing from pressure release, which created secondary porosity and permeablity. Gauthier-Lafaye and Weber (1989) suggest that mixing of the uranium-bearing oxidized fluids with more reducing fluids (associated with hydrocarbons) resulted in the precipitation of uraninite.

The ores from reactor zones within the deposit are described as being different from other ore deposits in the Franceville basin (Gauthier-Lafaye et al., 1989), in that the former commonly contain between 20 and 60 percent uranium as opposed to a few percent in the "normal" ores. The uranium is hosted by "well-crystallized cubic uraninite" as opposed to pitchblende in the normal ores. The reactor ores are surrounded by an argillaceous matrix which contains clay minerals that grade from 1M illite and dioctahedral Mg-Al chlorite within the orezone, to an alteration halo of Mg-chlorite, followed by $2M_1$ illite 0.5 to 2 m from the core. The surrounding sandstones have low uranium abundances with normal ratios of $^{235}U/^{238}U$ and contain $1M_d$ illite and Fe-chlorite as clay minerals (Gauthier-Lafaye et al., 1989). The structural polytypes of illite are a function of temperature with the evolution from $1M_d$ to 1M to 2M ($2M_d$ or $2M_2$) occurring with increasing temperature (see for instance Percival, 1989). Gauthier-Lafaye et al. (1989) explain the problematic 1M illite in the core of the reactor as due to the inhibition of reaction to a higher polytype (and crystallinity) from the bombardment of neutrons and excessive reactivity of the reactors. Crystallization of the 1M illite in the reactor core after fission reactions subsided and at a lower temperature is supported by the oxygen isotope data. Gauthier-Lafaye et al. (1989) suggest from the textural evidence and oxygen isotopes of the clay minerals in the alteration halo, that the clays were a product of hydrothermal alteration of the sandstones.

The convective circulation of the hydrothermal fluids, driven by increased temperatures from fission reactions, resulted in silica depletion and concentration of uranium. The hydrothermal process maintained criticality by continuous enrichment of the reactor zones with uranium of a normal $^{235}U/^{238}U$ (Gauthier-Lafaye, 1989). The hydrothermal fluids may also have been important as a moderator for the nuclear fission reactions (Brookins, 1990). Temperatures and pressures of the circulating fluids have been suggested from fluid inclusion studies and petrologic evidence as 120-140°C, 270-320 bars, and salinity of ≈ 20 equivalent wt% NaCl for the fluids associated with the main mineralization (Gauthier-Lafaye and Weber, 1989), and temperatures between 450° and 600° and pressures around 1 kbar during the operative period of the nuclear reactors (Vidale, 1978; Openshaw et al., 1978).

Devillers et al. (1975) gives a Nd-Sm age of ≈ 2000 Ma and a U-Pb age of ≈ 1800 Ma for deposition of the uranium ores. U-Pb data from Gancarz (1978) yield a slightly higher age of 2050 Ma, with all samples showing evidence of lead loss (an average of 50%). Duration of criticality has been estimated at around 0.2 to 0.6 Ma (Cowan et al., 1975; Loubet

and Allegre, 1977; Hagemann et al., 1975; Curtis et al., 1986; Loss et al., 1988). Neutron fluence was on the order of 10^{20}-10^{21} neutrons/cm^2 (Loubet and Allegre, 1977; Ruffenbach et al., 1975; Loss et al., 1988).

Extensive work has been published on the retention and migration of radioactive, fission, and daughter products from the Oklo natural nuclear reactors. The results are summarized below.

escape from uraninite (largely from Cowan, 1978): by recoil damage (≈10%, distributed between light mass ≈90% and heavy mass ≈5% nuclides), by dissolution and reprecipitation (considered negligible based on ion probe data from Havette, 1978), and by diffusion (considered by Cowan, 1978 to be the dominant process).
retained quantitatively- Pd, LREE's, & Th (& may apply to Pu, Am, Cm)
retained nearly quantitatively- Nb, Zr, Ru, Ag, & Te, Sr & Ba between 0.1 and 10% retention, Mo ≈ 10% retention;
poorly retained (0.01-1%)- Kr, Rb, Xe (may also include Cs, Cd, & I), at least 75% lead has been lost, with perhaps as much as 10% secondary retention as galena in the gangue.

escape from ore zone (Walton and Cowan, 1975; Maeck, et al., 1975; Curtis et al., 1989):
migrated- Kr, Xe, Rb, Cs, Sr, Ba, I, & Mo (≈ 90% reported by Maeck et al., 1975);
quantitatively retained relative to Te (Curtis et al., 1989): Te (1), Ru (0.91), Pd (0.88), Nd (0.83), ^{126}Te-^{126}Sn (0.80), Ce (Maeck et al., 1975);
partially retained relative to Te (Curtis et al., 1989): ^{99}Ru-^{99}Tc (0.66), Ag (≤0.34), Mo (0.26), Sn (≥0.26), & Cd (0.002);

escape from peripheral rocks (Loss et al, 1989):
most retained- Mo, Te;
some retained- Tc, Pd, Ag, Sb, Ru;
none retained- Cd.

Brookins (1981) argues for retention of "an unknown, but possibly large quantity" of Rb & Sr in the peripheral rocks of the ore zones. Arguments for the retention of Cs (for ≈ 25 Ma after reactor shutdown)

were also advanced by Brookins (1990) based on a positive correlation between $^{137}Ba/^{135}Ba$ and total U fission.

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